Journal of Applied Sciences

ISSN 1812-5654

science alert

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Journal of Applied Sciences 10 (12): 1116-1121, 2010
ISSN 1812-5654

Study of Changes in a Palm-Shell-Based Activated Carbon Characteristics by Nitric Acid

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Abstract: A palm-shell-based activated carbon (PSAC) was oxidized with nitric acid solutions at different conditions. A 2-level full factorial design was considered for experimental conditions. Adsorption of nitrogen at 77 K, and Temperature-Programmed Desorption (TPD) were used to study the oxidized PSAC. Although, oxidation by nitric acid decreases the surface area and pore volume of PSAC, however it creates a considerable amount of different oxygen groups on the surface of PSAC.

Key words: Palm-shell-based activated carbon, surface oxidation, nitric acid

INTRODUCTION

Nowadays Activated Carbon (AC) may be used as adsorbent, catalyst and catalyst support due to their high surface area, chemical activity and also the capability of tailoring their surface chemistry.

Depending on the precursor of AC, it may have an amount of functional groups of different types and densities. ACs prepared from coal, petroleum, coke, wood, fruit stone, coconut shell and so on, have mainly oxygen-containing functional groups. With precursors such as nitrogen-enriched polymers (Bandosz and Ania, 2006), urea-formaldehyde and melamine formaldehyde (Drage *et al*., 2007) the produced ACs have a considerable amount of nitrogen surface groups.

Oxidation as a common method to create oxygen functional groups on the surface of AC may be regarded as an important procedure for modification of AC surface. The reason lies on the fact that not only oxidation may be used as final functionalization for some applications, but also they may be used as preliminary surface treatment for a further functionalization. As examples for the former case, acidic groups favour catalytic wet air oxidation of aniline (Gomes *et al*., 2008) and improve adsorption of metallic ions and metallic species from solution. On the other hand, in the case of anchoring different organic molecules such as diamines (Silva *et al*., 2007; Tamai *et al*., 2006; Gorgulho *et al*., 2008) and aminosilanes (Silva *et al*., 2007; Matsuo *et al*., 2008, 2007), oxidation is considered as a preliminary modification. Oxidation is usually categorized to dry and wet processes (Gomez-Serrano *et al*., 2002). In dry oxidation, an oxidizing gas such as steam, oxygen, carbon dioxide, ozone at an elevated temperature (>700°C) is used, while wet oxidation is performed by a liquid oxidizing agent at mild temperature (20-100°C). There are a variety of liquid oxidants; but the ones, most reported in the papers are nitric acid, sulphuric acid, hydrogen peroxide and ammonium persulfate.

Type of oxidant, its concentration and time and temperature of oxidation specify the severity of oxidation and determine the effects on AC texture and chemistry. It is noteworthy that origin and history of preparation and activation of a carbon material affect the extent of changes on AC. Therefore, it is rational that discrepant results are reported for effects of oxidation. For instance, some researchers reported that wet oxidation decrease surface area of AC (El-Sheikh, 2008; Derylo-Marczewska *et al*., 2008; Ania *et al*., 2002; Salame and Bandosz, 1999; El-Sayed and Bandosz, 2001, 2004), while some others reports show constant or increased surface area (Jansen and van Bekkum, 1994; El-Sayed and Bandosz, 2004, 2001; Domingo-Garcia *et al*., 2000; Julien *et al*., 1998; Figueiredo *et al*., 1999). It was reported that if AC is activated in low temperature, it can get more serious changes in structure by oxidation, compared to AC activated in high temperature (Salame and Bandosz, 2001), because the former is subjected to destruction upon oxidation (Jansen and Van Bekkum, 1994). On the other hand, the above-mentioned parameters, also affect the type and density of created oxygen groups. Nitric acid treatment is probably a good way to increase carboxylic and phenolic groups in higher order as reported by researchers (Strelko *et al*., 2002; Pittman *et al*., 1997). Palm

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shell as a biomass solid waste is a suitable source for preparation of AC in countries such as Malaysia (Jia and Lua, 2008; Guo and Lua, 2002). Understanding behaviour of Palm-shell-based activated carbon upon nitric acid is the objective of this study.

MATERIALS AND METHODS

Materials: The palm-shell-based activated carbon (PSAC) used in this study was supplied by BRAVOGREEN SDN BHD. It was sieved to the size range of 500-850 micron (µm), washed with distilled water to remove fines, dried in an oven at 110 °C overnight and kept in closed bottles for experiment (designated as AC01). Reagent-grade nitric acid was obtained from Fisher Scientific, Malaysia.

Oxidation methods: Experimental conditions were specified by using a two factorial method so that the low and high level values for oxidation conditions were 2 and 8 (Eq L^{-1}) for concentration, 25 and 70 °C for temp 2 and 8 h for reaction time. The conditions of the designed experiments along with their adopted designations are shown in Table 1. For each oxidation experiment, a specified amount of untreated AC was reacted the acidic solution of adjusted concentration in a jacketed (double-walled) glassy reactor. A constant-temperature water stream was circulating in the jacket of reactor to maintain the reactor contents at the desired temperature. A polymer coated magnetic stirrer was used to mix the content of the reactor. After oxidation finished the oxidized PSAC was washed extensively with distilled water. The product was, then, dried in an oven overnight and kept in closed bottle for analysis.

Characterization methods

Textural characteristics: To measure textural characteristics of the parent sample and the oxidized ones, physical adsorption-desorption of nitrogen at 77 K by ASAP 2020, Micromeritics was utilized.

BET surface area (S_{BET}) was obtained based on adsorption data in the relative pressure (P/P_0) range of 0.01 to 0.3 and total pore Volume (V_t) was considered at P/P_0=0.995. Micropore volume (W_0) was calculated using Dubinin-Radushkevich (DR) equation.

Table 1: Designed experiments and their adopted designations

No.	Experiment designation	Concentration (Eq L^{-1})	Temperature (°C)	Time (h)
1	NC2T25H2	2	25	2
2	NC2T25H8	2	25	8
3	NC2T70H2	2	70	2
4	NC2T70H8	2	70	8
5	NC8T25H2	8	25	2
6	NC8T25H8	8	25	8
7	NC8T70H2	8	70	2
8	NC8T70H8	8	70	8

Surface chemistry: To study chemistry of activated carbon surface, Temperature-Programmed Desorption (TPD) was employed by using Chemisorb 2720 (Micromeritics). Flow rate of He and temperature ramp were 25 mL min^{-1} and 5°C min^{-1}, respectively. Thermo Conductivity Detector (TCD) signal of the apparatus was monitored and recorded to explain AC surface chemistry.

RESULTS AND DISCUSSION

Textural characteristics: Nitrogen adsorption-desorption isotherms at 77 K for samples oxidized by 2 and 8 N nitric acid are shown in Fig. 1 and 2, respectively. For ease of comparison, the isotherm of not-oxidized sample is shown in both figures. According to IUPAC classification, all the

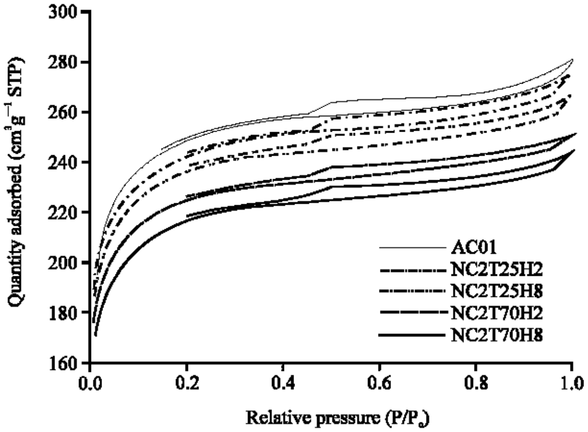

Fig. 1: Adsorption isotherms of samples oxidized by 2 N nitric acid

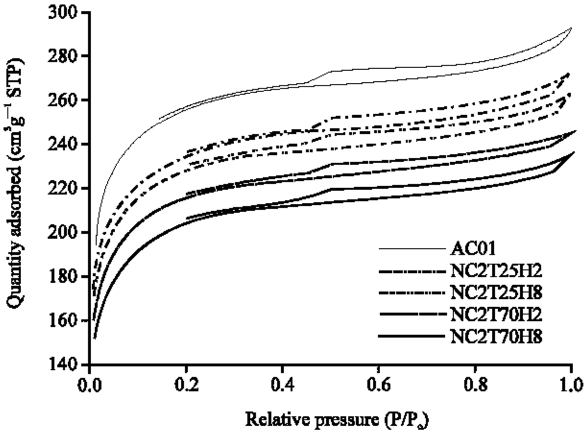

Fig. 2: Adsorption isotherms of samples oxidized by 8 N nitric acid

isotherms are type I and indicate a It can be seen from the figures that the volume of dominant microporous structure. However, the presence of mesopore in the structure of all samples is proved by the hysteresis loops. adsorbed nitrogen and consequently the surface area of all oxidized samples have been decreased, compared to the untreated sample AC01. However, the extent of decrease is diverse for different samples, depending on severity conditions. As indicated by the figures, an increase in acid concentration, temperature and time cause more decrease in surface area.

Some textural characteristics of the samples are shown in Table 2, as it can be seen from this table, BET surface area, the total pore volume (V_t) and DR micropore volume (V_{mic}) decrease with increase in one or more of severity parameters. Different reasons may cause the decrease in S_{BET}, V_t and V_{mic} (Alvarez *et al*., 2005; Gorgulho *et al*., 2008; Jansen and Van Bekkum, 1994; El-Sayed and Bandosz, 2001; Strelko *et al*., 2002; El-Hendawy, 2003; Szymanski *et al*., 2004; Li *et al*., 2003; Moreno-Castilla *et al*., 1997; Strelko and Malik, 2002; Maroto-Valer *et al*., 2004). The most important ones are destruction of micropores and pore blockage by created oxygen groups.

The percentage of decrease in S_{BET} relative to parent sample is also indicated in Table 2. Based on this column, we can obtain the degree of oxidation severity of all oxidized samples as shown in the last column. A larger number indicates a higher degree of oxidation. It is noteworthy that surface area, the total pore volume and V_{mic} of oxidized samples suggests the same order of oxidation.

Surface chemistry: When AC is heated under an inert gas atmosphere, oxygen functional groups are decomposed and desorbed from the surface of AC as CO_2 and CO, mostly at temperatures up to 100°C (Otake and Jenkins, 1993). Decomposition temperatures and desorbed volume depend on type of oxygen groups and their density on the AC surface, respectively. Carboxylic groups and lactones decompose as CO_2 at lower and higher temperature, respectively, while phenol, carbonyl, ether and quinine originate CO. And carboxylic anhydride groups release both CO and CO_2, simultaneously (Radkevich *et al*., 2008; Lemus-Yegres *et al*., 2007; Pereira *et al*., 2003) or consecutively (Aksoylu *et al*., 2001; Zielke *et al*., 1996). TPD assignment temperatures found in the literature are to some extent discrepant.

Temperature ramp rate, the texture of AC (Figueiredo *et al*., 1999) and its heterogeneity (Zielke *et al*., 1996) and geometry of experimental apparatus (Figueiredo *et al*., 1999) affect TPD spectra.

Table 2: Textural characteristics of treated and untreated samples

Sample	SBET $(m^2 g^{-1})$	V_t	Vmic $(m^3 g^{-1})$	Decrease in SBET (%)	Order of oxidation severity
AC01	846.3	0.434	0.395	-	
NC2T25H2	786.3	0.426	0.384	7.1	1
NC2T25H8	767.1	0.412	0.376	9.4	2
NC2T70H2	727.6	0.387	0.356	14	3
NC2T70H8	703.1	0.376	0.344	16.9	6
NC8T25H2	722.5	0.387	0.354	14.6	4
NC8T25H8	716.9	0.38	0.351	15.3	5
NC8T70H2	670.1	0.354	0.328	20.8	7
NC8T70H8	639	0.34	0.312	24.5	8

Table 3: TPD assignment temperatures

Evolved gas	Type of oxygen groups	TPD temperature assignment (°C)
CO_2	Carboxylic	200-500 (Stavropoulos *et al*., 2008)
	Lactones	370-670 (Radkevich *et al*., 2008), 627 (Figueiredo *et al*., 1999; Tseng and Wey, 2006)
	Carboxylic Anhydrides	370-670 (Radkevich *et al*., 2008), 600 (Figueiredo *et al*., 1999; Tseng and Wey, 2006)
	Peroxide	550-600 (Zielke *et al*., 1996)
CO	Carboxylic Anhydrides	370-670 (Radkevich *et al*., 2008), 400-577 (Lemus-Yegres *et al*., 2007)
	Phenol	600-700 (Lemus-Yegres *et al*., 2007, Zielke *et al*., 1996, Figueiredo *et al*., 1999; Tseng and Wey, 2006; Aguilar *et al*., 2003)
	Carbonyl	800-900 (Lemus-Yegres *et al*., 2007, Zielke *et al*., 1996; Figueiredo *et al*., 1999; Tseng and Wey, 2006)
	Ether	700 (Figueiredo *et al*., 1999), 800-900 (Tseng and Wey, 2006)
	Quinone	700-980 (Figueiredo *et al*,. 1999; Tseng and Wey, 2006), 800-900 (Zielke *et al*., 1996; Figueiredo *et al*., 1999; Tseng and Wey, 2006)

Table 3 shows some TPD assignment temperatures. Due to interaction with neighbourhood groups (Contescu *et al*., 1997; Gorgulho *et al*., 2008), carboxylic groups may show a wide range of acidity (Stavropoulos *et al*., 2008; Moreno-Castilla *et al*., 2000; Contescu *et al*., 1997). TPS spectrum may also have H_2O, which may be attributed to physisorbed water or H-bound water associated to oxygen groups (Otake and Jenkins, 1993; Toumi *et al*., 2006). TPD spectra of the samples have been shown in Fig. 3 and 4.

Nitric acid treatment increases the height of some peaks and creates new peaks and shoulders. By overlaying TPD spectra of all the samples, eight temperatures regions of gas evolution may be distinguished, as shown in Table 4, the first peak at temperatures between 55-70°C is probably related to physisorbed water. The second and third regions of gas evolution are probably stemmed from decomposition of carboxylic groups. However, it is difficult to attribute the other regions to specific oxygen groups. This can be seen from the temperature assignment indicated in Table 3.

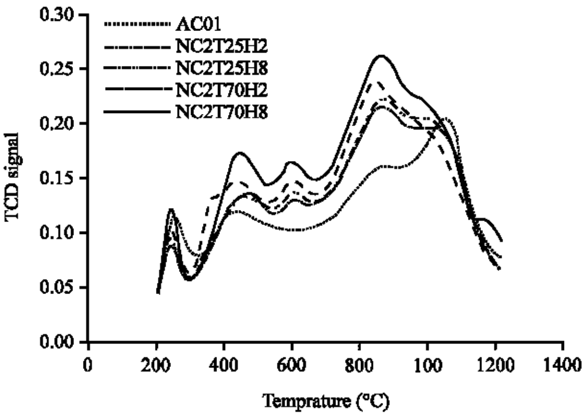

Fig. 3: TPD spectra of the samples oxidized by 2 N nitric acid

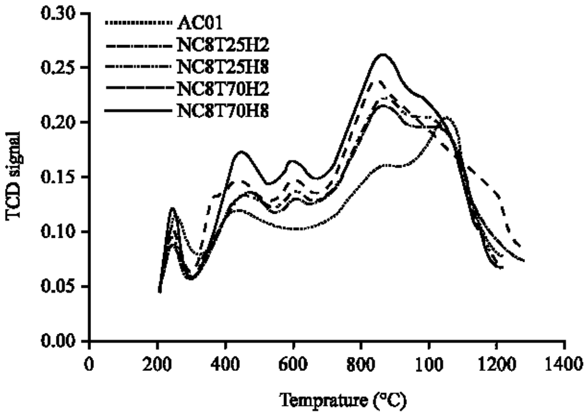

Fig. 4: TPD spectra of the samples oxidized by 8 N nitric acid

Table 4: Temperature regions of peaks and shoulders for the samples

Peaks	Temperature regions
1	56-71
2	170-185
3	235-280
4	407-420
5	650-680
6	750-785
7	850-870
8	955-965

Table 5: Area below curve (abc) of tpd spectra of the samples

Sample	ABC	Increase in ABC (%)	Order of oxidation severity
AC01	73.6	-	-
NC2T25H2	87.3	18.6	1
NC2T25H8	90.5	22.8	2
NC2T70H2	96.3	30.7	3
NC2T70H8	109.5	48.7	6
NC8T25H2	99.1	34.5	4
NC8T25H8	107	45.3	5
NC8T70H2	115.2	56.5	7
NC8T70H8	130.1	76.7	8

The area below curve (represented here as ABC) of TPD spectra may be used as an index of oxidation. A higher ABC index indicates amore degree of oxidation. This index is shown in Table 5, the percentage of increase in ABC and the degree of oxidation severity accordingly are also shown: Increasing in nitric acid concentration, time or temperature increase the amount of ABC and subsequently density of oxygen groups. As it can be seen from the right columns of Table 2 and 5, conditions of oxidation by nitric acid have the same order of effects on texture and surface chemistry of PSAC. This fact suggests that the increase in surface oxygen groups and the decrease in surface area are probably occurred due to the same reason(s).

CONCLUSION

PSAC was oxidized by nitric acid at different conditions. Although increase in surface area and/or pore volume upon oxidation by nitric acid has been reported for several types of AC, this study showed that the used PSAC loses its surface area and pore/micropore volume after oxidation by nitric acid, even at mild severity of oxidation. It was also shown that nitric acid creates a considerable amount of oxygen functional groups, especially the acidic ones. The obtained results, however indicate that the effects of oxidation severity on texture and surface chemistry of PSAC follow the same trend.

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